

SYMPOSIUM ON PYROLYSIS REACTIONS OF FOSSIL FUELS
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THE EFFECT OF STRUCTURE ON THE RATES OF PYROLYSIS
OF NAPHTHENES

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INTRODUCTION

The Air Force is considering the use of vaporizing and endothermic fuels for cooling high-speed aircraft in the range Mach 3 to about 10. In our work on this problem, as reported in previous papers, (1, 2) we have shown how the endothermic portion of the heat sink can be provided through catalytic dehydrogenation reactions of, particularly, naphthenes. Also, some heat sink can be obtained through thermal cracking reactions. In any event, pyrolysis can be expected to occur in any system in which hydrocarbons are heated up to 1400°F or higher. Accordingly, we have investigated the pyrolytic reactions undergone by all hydrocarbons we have attempted to react catalytically. In this paper we present the results of these studies on naphthenic hydrocarbons. The emphasis here is on the relative rates of the thermal reaction of the various naphthenes rather than the heat sinks obtainable from them.

Methylcyclohexane (MCH), ethylcyclohexane (ECH), the three dimethylcyclohexane (DMCH) isomers, a mixture of the three diethylcyclohexane isomers (DECH), dicyclohexyl (DCH) and a mixture of decalin and methylcyclohexane were tested at 10 atm pressure in the temperature region of 900-1300°F. First-order rate constants were calculated, based on the rate of disappearance of the starting material according to the following equation:*

$$K_{\text{sec-1}} = \frac{\text{LHSV}}{3600} \times \frac{\rho \times 22,412}{\text{MW} \times P} \times \frac{T}{273} \times 2.3 \log \frac{1}{1-f} \quad (1)$$

where

- LHSV = liquid hourly space velocity (i. e. , volumes of feed/volumes of "catalyst" per hour)
- MW = molecular weight
- P = reactor pressure in atmospheres
- T = reaction temperature in °K (block temperature)
- ρ = density
- f = fraction reacted.

Relative reactivities and activation energies were computed from these first-order rate constants.

Liquid products were analyzed by GLC and were found to be mainly cracked material with small amounts of dealkylated aromatics and unidentified material that was heavier than the feed. The light gas products were analyzed by mass spectrometry and were found to be mainly methane with lesser amounts of hydrogen, ethane, ethylene and C₃ and C₄ hydrocarbons.

The apparatus was a tubular flow reactor equipped with conventional devices for measuring feed flow rates and for collecting liquid and gas products. The reactor was a stainless steel tube (No. 347, 1/2-inch IPS) 32 inches long and was heated by an electric furnace. The complete apparatus was described in detail in the previous papers. (1, 2) For the thermal tests 20 ml of quartz chips (10-20 mesh) were substituted for the catalyst; the "catalyst bed"

*A more intricate method for calculating rate constants for reaction of starting material to gas, liquid, and liquid residues has been proposed by Fabus (3) et al which is particularly applicable to the batch conditions under which they conducted their studies. Our method is patently not strictly accurate since we neglect the volume occupied by the space filler (quartz chips) and ignore the fact that a number of moles of product are generated in the reactor which has the effect of reducing contact time. We also ignore the possibility that reaction can take place before and after the quartz chip bed.

was 3/16 in. annular thickness and about 5 in. long.

Feed materials were:

Methylcyclohexane: Phillips' pure grade passed over silica gel prior to use. Analyzed 99+ % MCH.

Ethylcyclohexane: Matheson, Coleman and Bell, practical grade; passed over silica gel prior to use. Analyzed 97.7% ECH, 2.3% MCH.

Dimethylcyclohexane: The DMCH isomers were prepared by hydrogenation of the corresponding xylenes. The various isomers had the following cis and trans composition:

	<u>1,4-DMCH</u>	<u>1,3-DMCH</u>	<u>1,2-DMCH</u>
% trans	32.1	31.8	40.8
% cis	67.6	68.2	57.8
trans/cis feed	0.475	0.456	0.706
trans/cis equil (1200°F)	1.57	0.645	2.13

Diethylcyclohexane: A Shell Chemical Company preparation containing a mixture of the three isomers and their cis and trans species with the following composition:

	<u>1,4-DECH, %</u>	<u>1,3-DECH, %</u>	<u>1,2-DECH, %</u>
trans	16.2	16.6	6.0
cis	13.4	38.2	9.6
total	29.6	54.8	15.6

Dicyclohexyl: Prepared by hydrogenation of diphenyl. Contained 1.6% phenylcyclohexane.

Decalin: Eastman Kodak practical grade. Contained about 1% of tetralin. Passed over silica gel prior to use.

RESULTS AND DISCUSSION

Conversions as a function of temperature for reaction of the various naphthenes are shown in Table 7, which also shows the yield of liquid and gas products. Complete data for the various naphthenes are shown in Tables 1 to 6, inclusive. Ethylcyclohexane was the most reactive naphthene at 1202°F and over 50% of the starting material was converted compared to 43.7%, 27.3%, and 20.6% for DECH, DMCH (average), and MCH, respectively. First-order rate constants were calculated from the conversions and are also tabulated in Table 7 and plotted as a function of $1/T$ in Figures 2 and 3. Relative reactivities of the various naphthenes at 1202°F (basis MCH = 1.00) were obtained from these rate constants and are presented in Table 8. Based on these values the relative naphthene reactivities are: ECH > DECH > DCH > DMCH > MCH. This suggests that addition of side chains to the naphthene ring enhances the reactivity for thermal reaction. Further, it appears that naphthenes with side chains containing two carbon atoms are more reactive than those with a side chain containing a single carbon atom.

With DMCH the position of the side chains and their trans-cis arrangement did not appear to influence the reactivity except for the trans 1,3- species. For example, at 1202°F the rate constants for the various isomers and their cis and trans species ranged from 0.091 to 0.10 except for the trans 1,3- species which was 0.053 (Table 3). Further, the evidence is that trans-cis isomerization was not extensive with the 1,4- and 1,2- isomers. This conclusion is based upon the observation that with these two isomers the trans/cis ratios of the feeds and products were about the same and were far from equilibrium (Figure 1, Table 3). For the 1,3- isomer the trans/cis ratios of the feed and product were about the same but were fairly close to the equilibrium value. Hence, no conclusions as to the isomerization rates can be made for this naphthene isomer but they would not be expected to differ much from the other isomers. The equilibrium values were calculated from the data of American Petroleum Institute, Research Project 44.

For DECH the reactivities of the three isomers decreased in the following order: 1,3 > 1,4 > 1,2 (Table 8). For the 1,3 and 1,4 isomers there was no effect of cis-trans arrangement on reactivity for a given isomer (Table 4). For the 1,2- species the trans species was considerably less reactive than the cis. The fact that the trans 1,3-DMCH species and the trans 1,2-DECH species appeared to be more stable than the other species under our conditions is simply an environmental accident, since the fact that their activation energies are higher requires that at some higher temperature they will react more rapidly (in this case this temperature is about 1350°F).

Activation energies were calculated for the various naphthenes and their isomers using the calculated rate constants. These values ranged from 35.0 to 70.0 kcal/mole (Table 8,

Table 1. THERMAL REACTION OF METHYLCYCLOHEXANE

"Catalyst": Quartz Chips
 "Catalyst" Volume: 20 ml
 Reaction Time: 20 min
 Pressure: 10 atm
 LHSV: 20

Run No.	8546-57	9426-51	9426-52
Temperature, °F			
Block	1112	1202	1295
Wall	-	1188	1256
"Catalyst" Bed	1067	1152	1191
Product Components, %			
MCH	88.8	79.4	52.3
Benzene	0.1	0.7	3.1
Toluene	0.2	0.4	2.2
Cracked, liquid	8.2	7.3	13.6
Cracked, gas	-	4.6	17.7
Heavier than Toluene	-	-	0.6
Others ^{a)}	2.8	7.7	10.5
MCH Conversion, %	11.2	20.6	47.7
First-Order Rate Constant, sec ⁻¹	0.04	0.08	0.22

a) Methylcyclohexenes, methylcyclohexadienes.

Table 2. ETHYLCYCLOHEXANE

Pressure: 10 atm
 LHSV: 20
 "Catalyst" Volume: 20 ml
 "Catalyst": Quartz Chips
 Reaction Time: 20 minutes
 Feed: 97.7% ECH, 2.3% MCH

Run No. 8957-	37	38-1	38-3	39
Reaction Time, min	20	20	20	20
LHSV	20	20	20	20
Temperature, °F				
Block	932	1022	1112	1202
Wall	932	1020	1108	1194
Catalyst	932	1020	1106	1188
Product Analysis, %				
Ethylcyclohexane	97.4	91.9	80.1	47.3
Ethylcyclohexene	-	-	-	-
Benzene	0.1	0.3	0.7	3.9
Toluene	-	-	0.1	1.8
Xylene	-	-	0.4	0.9
Ethylbenzene	-	-	-	0.5
Styrene	-	-	0.1	0.6
Cracked Products	2.3	3.7	12.7	25.0
Light gas	-	4.1	6.1	19.8
ECH Conversion, %	2.6	8.1	19.9	52.7
Rate Constant, sec ⁻¹	-	0.012	0.066	0.26

Figure 2). There was no general correlation between reactivity and activation energy, i. e., frequency factors also varied for different naphthenes. These values of the activation energies showed greater spread than was observed by Fabus et al. (4) These workers found that in a static system at 750 to 850°F and at 130 atm pressure most of the activation energies ranged between 60 and 65 kcal.

Curiously, the ethyl derivatives (with the exception of trans 1, 2) and DCH all had energies of activation closer to that of MCH than did the dimethyl derivatives, all of which had E's substantially greater than MCH.

Typical gas-phase product distributions are tabulated in Table 9 for reaction at 1202°F. In all cases the principal product was methane with lesser amounts of hydrogen, ethane, and ethylene. Since with ECH and DECH the sum of the ethane plus ethylene was greater than or equal to the methane formed while with MCH and DMCH the sum of the C₂ components was considerably less than the methane, it is apparent that dealkylation of the side chain is one of the important reactions during pyrolysis of alkyl naphthenes.

CONCLUSIONS

1. The average rate of pyrolysis of naphthenes is $K = 0.1 \text{ sec}^{-1}$ at about 1180°F.
2. The average energy of activation is about 50 kcal/mole, but values range from 37 to 70.
3. Activation energies are generally higher for the dimethyl derivatives than for the ethyl derivatives or MCH or DCH.
4. The highest activation energies are for two trans derivatives, 1, 3-DMCH or 1, 2-DECH.
5. Generally the position of methyl groups does not affect rates while that of ethyl groups does.
6. Both ring and side chain cracking occurs during pyrolysis.

ACKNOWLEDGMENT

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Table 3. THERMAL REACTION OF DIMETHYLCYCLOHEXANE ISOMERS

"Catalyst": Quartz Chips "Catalyst" Bed Thickness: 3/16 in.
 "Catalyst" Volume: 20 ml Pressure: 10 atm
 "Catalyst" Size: 10-20 mesh Reaction Time: 20 min
 LHSV: 20

Run No.	81	82	83-1	83-3	93	94-1	94-3	95	99	100-1	100-3	101
Isoner % trans % cis Trans/cis, feed Trans/cis, equil (1200° F)			1,4-DMCH 32.1 67.6 0.475 1.57			1,3-DMCH 31.1 68.2 0.456 0.645				1,2-DMCH 40.8 57.8 0.706 2.13		
Temperature, °F												
Block												
Wall												
"Catalyst" Bed												
Product Analysis, %												
trans DMCH	932	1022	1112	1202	932	1022	1112	1202	932	1022	1112	1202
cis DMCH	927	1017	1108	1188	927	1017	1108	1190	930	1020	1108	1191
Benzene	898	990	1082	1143	896	986	1076	1141	909	1000	1082	1144
Toluene	31.8	31.9	30.7	22.7	31.1	31.0	30.5	25.4	40.8	40.6	38.4	29.7
Xylene	67.9	67.4	64.7	48.5	67.8	67.8	64.8	49.1	57.6	57.2	54.2	40.6
Cracked, liquid ^{a)}	0.0	0.0	0.0	1.8	0.0	0.0	0.0	1.1	0.0	0.0	0.6	2.3
Cracked, gas	0.0	0.0	0.0	1.4	0.0	0.0	0.0	1.0	0.0	0.0	0.1	1.8
Others	0.4	0.4	0.4	0.7	0.0	0.0	0.0	0.2	0.3	0.3	0.1	0.4
Trans/cis, products	0.0	0.1	2.7	10.5	0.1	0.1	2.4	9.5	1.2	2.0	6.5	16.5
Conversion, %	0.0	0.0	0.0	10.5	0.0	0.0	7.9	0.0	0.0	0.0	0.0	10.0
trans DMCH	0.0	0.2	1.4	3.8	1.1	1.1	2.3	4.5	0.0	0.0	0.3	0.6
cis DMCH	0.468	0.473	0.474	0.468	0.452	0.452	0.470	0.518	0.71	0.71	0.71	0.73
Total	0.0	0.6	4.3	29.2	0.0	0.5	2.0	16.8	0.0	0.3	6.0	27.8
First-Order Rate	0.0	0.3	4.3	28.2	0.7	0.7	5.0	28.1	0.4	1.2	6.4	30.5
Constant, sec ⁻¹	0.0	0.4	4.3	28.5	0.4	0.5	4.0	24.5	0.3	0.9	6.2	28.8
trans	-	-	0.012	0.099	-	-	0.006	0.053	-	-	0.017	0.091
cis	-	-	0.012	0.098	-	-	0.014	0.094	-	-	0.018	0.104
Total	-	-	0.012	0.098	-	-	0.011	0.091	-	-	0.017	0.10

a) lighter than DMCH.

Table 4. DIETHYLCYCLOHEXANE

Pressure:	10 atm	"Catalyst":	Quartz Chips
LHSV:	20	"Catalyst" Size:	10-20 Mesh
Reaction Time:	20 min	"Catalyst" Volume:	20 ml
Feed:	1,4-DECH, % 16.2 trans 13.4 cis 29.6 total	1,3-DECH, % 16.6 trans 38.2 cis 54.8 total	1,2-DECH, % 6.0 trans 9.6 cis 15.6 total

Reaction Data			
Run 8957-	125-1	125-2	126-1
Temperature, °F	1112	1202	1293
Block	1100	1180	1251
Wall	1056	1118	1159
Catalyst Bed			
DECH Conversion, %			
trans-1,4	11.8	42.6	72.8
cis-1,4	11.2	43.3	75.4
Total 1,4	11.5	42.9	74.0
trans-1,3	15.2	45.4	75.8
cis-1,3	18.1	46.2	75.1
Total 1,3	17.2	46.0	75.3
trans-1,2	3.4	31.7	65.0
cis-1,2	9.4	40.6	73.9
Total 1,2	7.1	37.2	71.2
Total DECH	14.0	43.7	74.1
Rate Constant, sec ⁻¹			
trans-1,4	0.029	0.133	0.321
cis-1,4	0.027	0.135	0.357
Total 1,4	0.028	0.134	0.347
trans-1,3	0.038	0.145	0.361
cis-1,3	0.046	0.149	0.354
Total 1,3	0.043	0.148	0.356
trans-1,2	0.008	0.054	0.267
cis-1,2	0.023	0.125	0.342
Total 1,2	0.017	0.111	0.317
Total DECH	0.035	0.136	0.344

a) UI = unidentified product.

Table 6. THERMAL REACTION OF DECALIN-METHYLCYCLOHEXANE MIXTURE

Feed:	Decalin, 22.1% MCH, 77.9%
Pressure:	10 atm
"Catalyst" Bed Thickness:	3/16 in.
"Catalyst":	Quartz Chips
"Catalyst" Volume:	20 ml
Reaction Time:	20 min
LHSV:	20

Run No. 8546-			
Temperature, °F	1022	1112	1202
Block	959	1051	1130
Catalyst			
Liquid Product Analysis, %			
MCH	76.8	74.4	64.0
cis-Decalin	11.8	11.7	8.3
trans-Decalin	8.9	9.0	7.0
Toluene	-	0.1	0.7
Benzene	-	0.1	0.8
Methylcyclohexenes	-	2.1	6.7
Naphthalene	-	-	0.1
Cracked, liquid	0.4	-	0.1
Cracked, light gas	0.2	0.9	4.0
First-Order Rate Constant, sec ⁻¹			
MCH	0.004	0.014	0.0638
Decalin	0.005	0.005	0.0990
Conversion, %			
MCH	1.4	4.5	17.9
Decalin	2.0	2.0	30.8

Table 5: THERMAL REACTION OF DICYCLOHEXYL

Pressure: 10 atm
 LHSV: 20
 Feed: 98.4% DCH
 1.6% PCH
 "Catalyst": Quartz chip
 "Catalyst" Volume: 20 ml

Run 9426-	Temperature, °F		Product Analysis, %					DCH Conversion, %	First-Order Rate Constant, sec ⁻¹
	Block	Wall	"Catalyst" Bed	DCH	PCH ^{b)}	Cracked, Liquid	Cracked, Light Gas	Others ^{a)}	
15	1022	1015	981	94.7	1.8	3.5	0.0	0.0	0.007
16	1112	1103	1060	88.1	1.5	10.3	0.0	0.0	0.023
17-1	1202	1186	1117	59.3	1.2	36.8	2.0	0.8	0.116
17-3	1293	1252	1157	31.7	1.4	50.4	14.2	2.3	0.267

a) Unidentified liquid product that emerged after DCH on GLC chromatogram.

b) Phenylcyclohexane.

Table 7. CONVERSION AS A FUNCTION OF TEMPERATURE

Pressure: 10 atm
LHSV: 20

Temperature, °F		Conversion, %	Product Yield, %		First Order Rate Constant, sec ⁻¹
Block	Wall		"Catalyst"	Liquid	
Methylcyclohexane					
1112	-	1067	11.2	0.0	0.04
1202	1188	1152	20.6	4.6	0.08
1293	1296	1191	47.7	50.0	0.22
Ethylcyclohexane					
932	932	932	2.6	0.0	-
1022	1020	1020	8.1	4.0	0.012
1112	1108	1106	19.9	13.5	0.066
1202	1194	1188	52.7	32.9	0.26
1,4-Dimethylcyclohexane					
1112	1108	1082	4.3	0.0	0.012
1202	1188	1143	28.5	18.5	0.098
1,3-Dimethylcyclohexane					
1112	1108	1076	4.0	0.0	0.011
1202	1190	1141	24.5	16.6	0.091
1,2-Dimethylcyclohexane					
1112	1108	1082	6.2	0.0	0.017
1202	1191	1144	28.8	18.6	0.10

(continued)

(continued)

Table 7 (contd). CONVERSION AS A FUNCTION OF TEMPERATURE

Temperature, °F		Conversion, %	Product Yield, %		First Order Rate Constant, sec ⁻¹
Block	Wall		"Catalyst"		
			Liquid	Light Gas	
Diethylcyclohexane Mixture					
1112	1100	1056	14.0	0.0	0.035
1202	1180	1118	28.9	14.8	0.136
1293	1251	1159	74.1	34.3	0.344
Diethylcyclohexane Isomers ^a					
1,4-DECH					
1112	1100	1056	11.5	-	0.028
1202	1180	1118	42.9	-	0.134
1293	1251	1159	74.0	-	0.345
1,3-DECH					
1112	1100	1056	17.2	-	0.043
1202	1180	1118	46.0	-	0.148
1293	1251	1159	75.3	-	0.356
1,2-DECH					
1112	1100	1056	7.1	-	0.017
1202	1180	1118	37.2	-	0.111
1293	1251	1159	71.2	-	0.317
Dicyclohexyl					
1022	1015	981	3.7	0.0	0.007
1112	1103	1060	10.3	0.0	0.023
1202	1186	1117	40.7	2.0	0.116
1293	1252	1157	68.3	14.7	0.267
Decalin (22% in Methylcyclohexane)					
1202	-	1130	30.8	-	0.099
Methylcyclohexane (76% in Decalin)					
1202	-	1130	17.9	-	0.0638

a) Computed from product analysis of runs with DECH mixture.

Table 8. THERMAL REACTION OF VARIOUS NAPHTHENES

Rate Constants and Activation Energies

"Catalyst": Quartz Chips
 Pressure: 10 atm
 "Catalyst" Volume: 20 ml

Hydrocarbon	Rate Constant, sec ⁻¹ (1202°F)	Activation Energy, kcal/mole	Relative Reactivity (MCH = 1.00; 1202°F)
MCH	0.08	39.3	1.00
1,4-DMCH	0.098	70.0	1.23
1,3-DMCH	0.090	66.0	1.13
1,2-DMCH	0.10	59.4	1.25
ECH	0.26	43.2	3.25
1,4-DECH	0.134	41.0	1.68
1,3-DECH	0.148	37.5	1.85
1,2-DECH	0.111	47.9	1.39
DCH	0.116	46.8	1.45
Decalin ^{a)}	0.099	-	1.24

a) 22% Decalin in MCH.

Table 9. GAS PRODUCTION AND COMPOSITION

Pressure: 10 atm
 Temperature: 1202°F
 LHSV: 20

Feed	MCH	ECH	1,4- DMCH	1,3- DMCH	1,2- DMCH	DECH	DCH	Decalin - MCH ^{b)}
Run No.	51	39	83-3	95	101	125-2	17-2	44
Feed Converted to Gas Products, %	4.6	19.8	10.5	7.9	10.0	14.8	2.0	4.0
Gas Products, %m								
H ₂	24.2	12.5	21.3	18.6	13.6	9.5	20.3	28.7
CH ₄	43.4	26.7	52.3	53.9	55.5	39.3	31.8	39.4
C ₂ H ₄	15.1	19.5	8.4	9.7	12.5	16.2	23.5	14.6
C ₂ H ₆	8.6	20.6	4.8	5.8	7.9	26.4	13.0	8.3
C ₃ H ₆	5.4	5.7	8.4	8.1	6.8	4.3	6.0	5.1
C ₃ H ₈	1.2	2.0	2.3	1.9	1.4	1.1	2.7	1.7
C ₄ H ₆	0.9	0.6	-	0.6	0.7	0.3	0.8	0.6
C ₄ H ₈	1.2	1.7	2.3	2.0	1.5	2.6	1.3	1.2
C ₄ H ₁₀	-	-	0.2	0.1	0.1	0.2	0.1	-
Others ^{a)}	0.2	0.6	-	-	-	0.4	0.4	-

a) Heavier than C₄.

b) 22% Decalin in MCH.

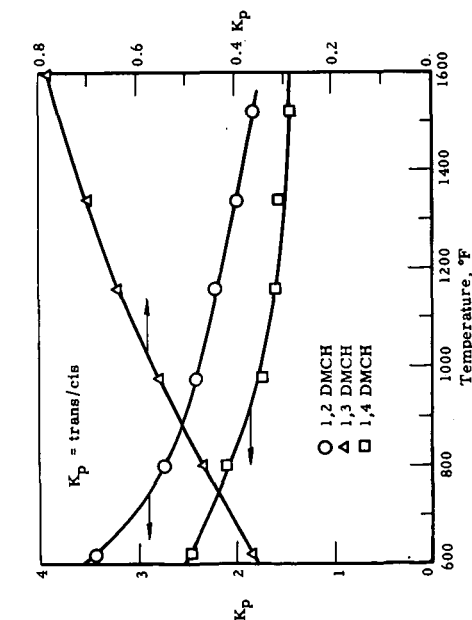


Figure 1. DIMETHYLCYCLOHEXANE TRANS-CIS EQUILIBRIA

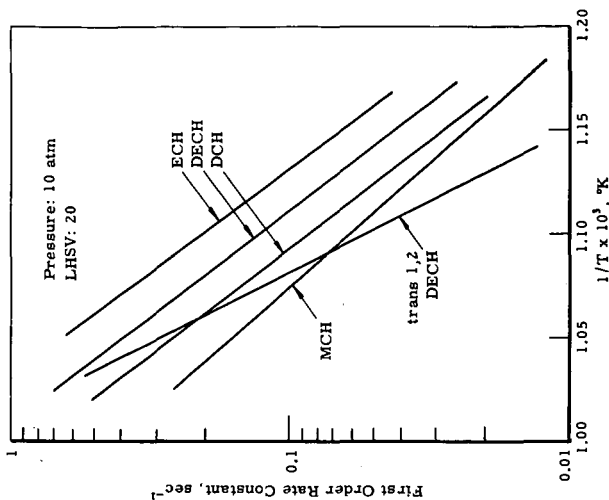


Figure 2. TEMPERATURE COEFFICIENT FOR THERMAL REACTION OF VARIOUS NAPHTHENES

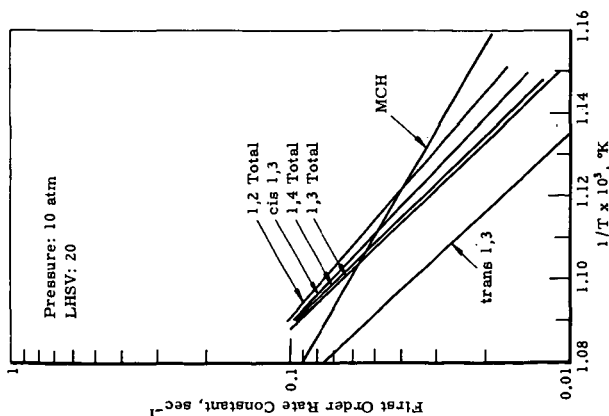


Figure 3. TEMP. COEFF. FOR THERMAL REACTION OF DIMETHYLCYCLOHEXANE ISOMERS